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(54) A porous membrane

(57) A porous membrane for separation of undissolved constituents from an aqueous medium comprises a support matrix (11a) with through-passages (22), an inner layer (11ba) of particles of aluminium hydroxide and/or at least partially hydrated aluminium oxide with a mean particle size exceeding 0.1 micron and an outer layer (11bb), of colloidal particles, substantially insoluble in the aqueous medium and with a mean size of less than 0.1 micron preferably, there is arranged between the inner and outer layer at least one intermediate layer (11bc) of particles of intermediate size. The layers are deposited on matrix 11a from successive slurries. The outer and intermediate layers may be oxides of Si, Ti or Zr. In Fig. 1, two such membranes are arranged in a cross-flow filter with a rubber-bladed rotor between them.

FIG. 4

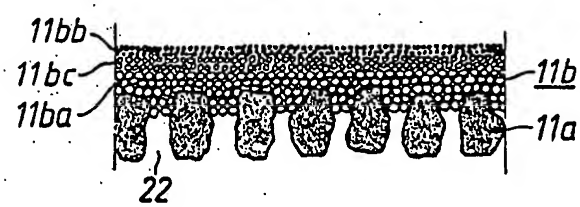

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FIG. 1

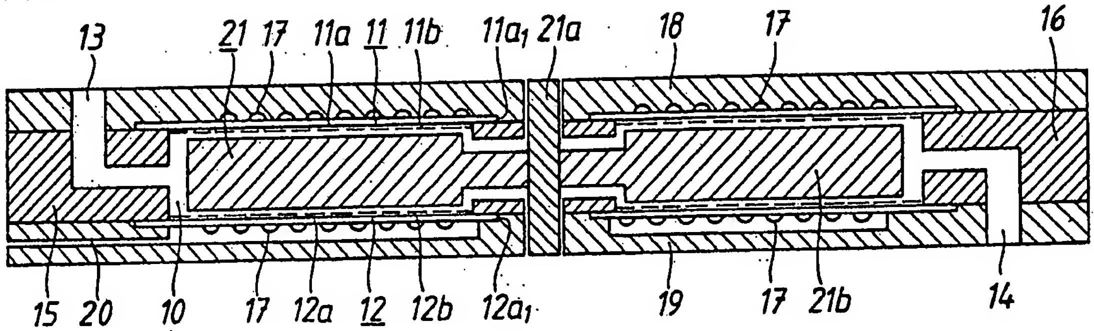


FIG. 2

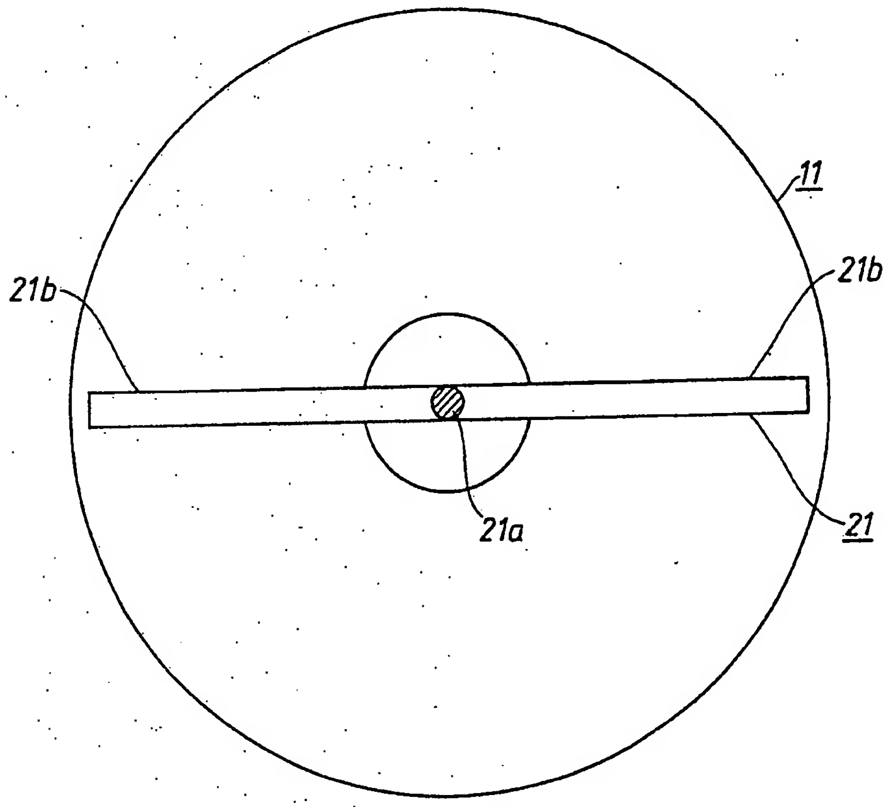


FIG. 3

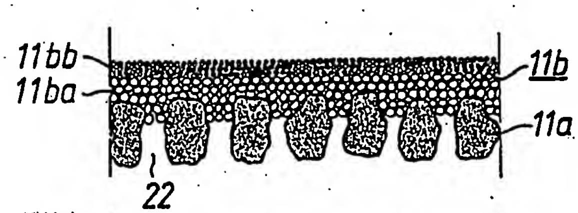
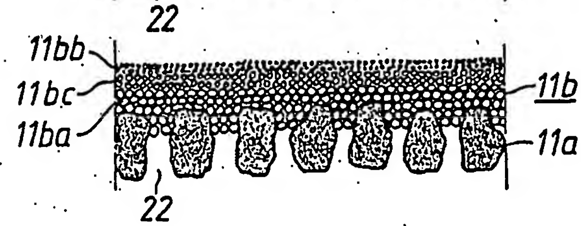


FIG. 4



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A Dynamic Membrane for Separation of a Liquid Medium at Least Substantially Consisting of Water

The present invention relates to a dynamic membrane for separation of a liquid medium, at least substantially consisting of water, from undissolved constituents therein, comprising a liquid-penetrable support matrix having through-passages therein, in which passages and on the surface of which matrix a layer of a particulate material is arranged.

A dynamic membrane according to this invention may be arranged in a separation device which, in addition to the dynamic membrane, comprises a chamber to which the liquid medium can be supplied on one side of the membrane. The layer of particulate material, which is small-sized, is porous with finer pores than the through-passages in the support matrix. In such a separation device, a supplied liquid medium, while maintaining a pressure in the chamber, may be led past the dynamic membrane and be divided into one flow - the permeate flow - which passes through the dynamic membrane, and another flow - the reject flow- which flows past the dynamic membrane. Separation devices based on dynamic membranes may be used for clarifying water with respect to undissolved liquid constituents, for example dispersed or emulsified oil, or undissolved solid particles, for example for separation of different types of slurries, such as a coal-water slurry, a peat-water slurry, and waste water from the production of cellulose.

When using a dynamic membrane, for clarifying a liquid, an increasingly thicker coating consisting of constituents undissolved in the liquid medium, is deposited, which successively reduces liquid flow through the dynamic membrane. Therefore, after some time in operation, the collected coating must be removed and either the layer of the small-sized particulate material be replaced by a new one, or the original properties of the membrane must be

restored in some other way. This regeneration of the membrane should preferably be carried out without dismantling the separation device. Up to the present time, regeneration has been effected by back flushing with a liquid or compressed air, or by dissolution or washing away of the coating and the particulate material in a liquid with a subsequent supply of a slurry of new particulate material to the matrix under such conditions that a fresh layer of the particulate material is deposited on the support matrix, and in the through-passages thereof. It is, of course, of vital importance to maintain as high a flow rate as possible through the membrane for as long a period of time as possible, so that any interruption in the filtration process for necessary regeneration of the membrane needs to be done quickly and/or at the greatest possible time intervals.

Silicon dioxide or zirconium dioxide is usually used as the small-sized particulate material in a dynamic membrane.

According to one aspect of the invention a dynamic membrane for separation of a liquid medium, at least substantially consisting of water, from undissolved constituents therein, comprises a liquid-penetrable support matrix with through-passages, in the passages of which and on the surface of which matrix there is arranged an inner porous water-holding layer of particles of aluminium hydroxide and/or particles of at least partially hydrated aluminium oxide with a mean particle size exceeding 0.1 micron and an outer layer, arranged outside the inner layer, of colloidal particles of a substance which is at least substantially insoluble in the liquid medium and has a mean particle size of less than 0.1 micron. The mean particle size in the inner layer preferably lies in the range 0.5 to 5 microns.

By "mean particle size" of a particulate material is

meant, in this specification, that particle size for which 50 per cent by weight of the particulate material has a smaller particle size and 50 per cent by weight of the particulate material has a larger particle size.

According to a specially preferred embodiment of the invention there is arranged, between the inner layer and the outer layer of particulate materials, at least one intermediate layer of particles of a substance which is at least substantially insoluble in the liquid medium and has a mean particle size which lies between the mean particle size of the particulate material in the inner layer and the mean particle size of the particulate material in the outer layer. The particulate material in an intermediate layer preferably has a mean particle size lying in the range of 0.1 to 0.5 micron.

The support matrix with through-passages may advantageously consist of a woven or felted product built up of fibres of a polymer material such as polyamide, polypropylene, cellulose acetate, polysulphone, polyethyleneglycol terephthalate, or polyurethane, or of fibres of a metallic material such as stainless steel, or of a natural fibre such as cotton. The support matrix may also consist of a sintered porous material with through pores. A porous plate of metal (such as stainless steel), or of a ceramic material (such as aluminium oxide) or a porous film of a polymer material, for example any of the above-mentioned polymer materials. The through-passages preferably have sizes in the range of 0.1 to 10 microns. The thickness of the support matrix may advantageously lie in the range 0.1 to 10 mm.

As will be clear from what has been said above, the particulate material in the inner porous layer may consist of aluminium hydroxide or hydrated aluminium oxide. The hydration may take place by the oxide itself taking up water on its surface. The pore size in the inner porous

layer preferably lies in the range 0.1 to 1 micron and the thickness of the layer advantageously lies in the range 5 to 100 microns. This inner layer is water-rich, has good penetrability to water and is hydrophilic.

The particulate material in the outer porous layer and in one or more possibly occurring porous intermediate layers may, inter alia, consist of an inorganic oxide such as an oxide of silicon, titanium, or zirconium, or of water insoluble inorganic salts, such as sulphates or carbonates, for example barium sulphate, calcium sulphate, barium carbonate, or calcium carbonate. The pore size in the outer porous layer preferably lies in the range of 0.005 to 0.1 micron and the thickness of the layer advantageously lies in the range of 1 to 20 microns. The pore size in any intermediate layer preferably amounts to 0.02 to 0.5 micron, and the thickness advantageously lies in the range of 1 to 20 microns. Outer layers and intermediate layers have a mechanically stabilizing effect on the inner, water-holding layer.

The outer layer is able to provide a very even surface, which reduces the risk of clogging of any solid particles. This applied particularly to cross-flow filtration. In separating oil from water, a very thin oil film is formed on the surface, which reduces the wear on the surface of the membrane, whereas oil never penetrates deeper down into the inner porous layer and blocks the passages or channels in the deeper parts which are available for liquid flow.

The outer layer is in itself hydrophilic but may be treated to give it a more or less hydrophobic surface if this is desirable from the point of view of the separation process to be conducted. A hydrophobic surface can be obtained by treating the particles or the finished layer formed from the particles with a wax or a silane.

A dynamic membrane according to the present invention is particularly suited for use when filtering in accordance with the cross-flow principle.

A particularly valuable property of a membrane according to the present invention is that, where necessary, it can be regenerated by scraping.

By use of the present invention, it has proved to be possible to provide a dynamic membrane through which a high flow rate can be maintained for a considerably longer period of time than has proved to be possible with prior art dynamic membranes. By first arranging on the support matrix an inner layer of a particulate material with the ability to retain water and then arranging outside this layer at least an outer layer of a particulate substance which is at least substantially insoluble in the liquid medium the particles in said outer layer having a smaller particle size than those forming the inner layer, the outer layer can protect the inner layer against clogging by undissolved constituents in the liquid medium.

A separation device incorporating a membrane in accordance with this invention represents a further aspect of the invention.

The invention will now be explained in greater detail, by way of example, with reference to the accompanying drawing, wherein

Figure 1 shows a separation device with a dynamic membrane according to the present invention in a section, perpendicular to the dynamic membrane, through the axis of a rotor in the separation device.

Figure 2 shows the dynamic membrane and the rotor of Figure 1 viewed in the direction of the rotor axis from the interior of the separation device, and

Figures 3 and 4 each show a cross-section of a small part of a dynamic membrane according to the present invention, on a considerably enlarged scale in two different embodiments.

The separation device shown in Figure 1 comprises a chamber 10 of cylindrical shape and two round dynamic membranes 11 and 12 are arranged at each of the two opposite end surfaces of the chamber. At their edges each membrane is sealingly attached to the walls of the chamber by seals (not shown). Each dynamic membrane consists of a porous matrix 11a and 12a, respectively, which can be a fine-meshed woven cloth with a central circular aperture $11a_1$ and $12a_1$, respectively, and of layers 11b and 12b, respectively, of a small-sized particulate material of the kind illustrated in Figures 3 and 4. At one point on the envelope surface, the chamber is provided with an inlet 13 for liquid medium which is to be treated in the separation device, and at a diametrically opposite point on the envelope surface the chamber is provided with an outlet 14 for the part of the supplied medium - the reject - which passes past the dynamic filters. The inlet 13 and the outlet 14 are arranged in the side walls 15 and 16 of the chamber. That part of the liquid in the supplied medium- the permeate - which passes through the dynamic membranes, flows into channels 17 in the walls 18 and 19 of the chamber, eventually passing to a permeate outlet 20.

A rotor 21 is arranged in the chamber 10, in the exemplified case comprising a rotor shaft 21a, the centre line of which coincides with the symmetry axis of the cylindrical chamber. Two wings or blades 21b of the rotor 21 are arranged in the chamber 10. The rotor shaft is journalled in the walls of the chamber by means of sealing bearings (not shown).

When the separation device is in operation, the liquid

medium with undissolved constituents to be subjected to clarifying is continuously led via the inlet 13 into the chamber 10 of the separation device. The liquid may, for example, consist of water containing oil drops and solid particles, such as oil-containing water from oil refineries or oil platforms, or waste water from workshops with cutting or grinding machines. The main part of the water passes through the dynamic membranes 11 and 12 as a permeate flow and can normally be led to a recipient via the outlet 20. The remaining liquid - the reject flow - is discharged via the outlet 14 and is returned to the polluted starting material or is subjected to an after-treatment which in most cases is simple. During the course of the process described, a pressure difference of preferably between 0.03 and 0.3 MPa is maintained between the media on either side of a dynamic membrane. The undissolved constituents which are successively accumulated on the dynamic membranes are removed by means of the rotor 21 when the coatings of the undissolved constituents constitute too great a resistance to the permeate flow for the separation to be carried out at a commercially satisfactory rate.

In the cases shown in Figures 3 and 4, the support matrix 11a consists of a fabric of polyamide, cross-sections of the fibres of which are shown in the Figures. The fabric has a thickness of 0.2 mm and the through passages 22 a size of 5 microns. The inner porous layer 11ba consists of particles of aluminium hydroxide with a mean particle size of about 1 micron. The thickness of the layer 11ba is on average 40 microns. The layer is applied on the support matrix by an aqueous suspension of $Al(OH)_3$ being sucked through the support matrix until the amount of $Al(OH)_3$ taken up by the support matrix amounts to 25 g/m^2. The aqueous suspension of $Al(OH)_3$ can be produced by suspending 6 parts by weight aluminium acetate in 100 parts by weight water containing hydrochloric acid to a pH of 1.5 and precipitation of the aluminium hydroxide under

vigorous stirring at a temperature below 50° with ammonia while adjusting the pH to 7.5. After that, in the case shown in Figure 4, an intermediate layer 11bc, consisting of particles of silicon dioxide with a mean particle size of 0.2 micron, is applied in an analogous manner by an aqueous suspension of such particles being sucked through the support matrix with an applied inner layer11ba until the absorbed quantity of SiO_2 amounts to 6 g/m² and the thickness of the porous layer 11bc thus formed amounts to about 10 microns. The aqueous suspension can be produced by mixing and shaking for 2 hours 250 parts by volume of water, 35 parts by volume of 25 per cent ammonia, 500 parts by volume of ethanol, and 120 parts by volume of tetraethyl orthosilicate and thereafter neutralizing the mixture to a pH of 7 with hydrochloric acid. Finally, the outer layer 11bb is applied on the support matrix 11a with the layer 11ba in the case according to Figure 3 and the layers 11ba and 11bc in the case according to Figure 4 by an aqueous suspension of silicon dioxide with a mean particle size of the particles of 0.08 micron being sucked through the support matrix until the quantity of SiO_2 absorbed by the support matrix amounts to 3 g/m² and the thickness of the layer amounts to 5 microns. This aqueous suspension of silicon dioxide can be produced by mixing 2 parts by volume of saturated ammonia hydroxide, 50 parts by volume of ethanol, and 4 parts by volume of tetrapenthyl orthosilicate. The application of the layers 11ba, 11bb, and 11bc can be carried out either before or after the support matrix has been placed in the separation device. It is possible to apply some of the layers, for example layers 11ba and 11bb, on the support matrix outside the separation device and one of the layers, for example layer 11bc, while the support matrix is located in the separation device.

As mentioned previously, the rotor 21 is used for removing coatings accumulated on the dynamic membranes. The wings 21b of the rotor are then used as scrapers. They are therefore made of a material which does not damage the

dynamic membranes, such as rubber, polytetrafluorethylene, or some other polymer material, and are arranged movable relative to the membranes in a direction perpendicular to the membranes. This movability can be achieved either by making the rotor shaft 21a with the rotor displaceable in a stationary chamber 10, or by making the chamber displaceable along a rotor arranged stationarily in the longitudinal direction of the rotor shaft.

The rotor can be utilized for regeneration of the dynamic membranes by bringing the rotor wings into contact with the layer 11b on the support matrix and displacing the wings along the support matrix. The layers 11bb and 11bc and possibly part of the layer 11ba are then suitably removed in connection with the removal of the coatings of the undissolved constituents of the liquid medium from the membranes. If required, particles of aluminium hydroxide are then applied on the support matrix using the previously described suspension in the manner previously described for restoring the layer 11ba. Thereafter, the layers 11bc and 11bb are applied in the above-described manner while using the above-described suspensions of silicon dioxide.

Instead of aluminium hydroxide the layer 11ba may be a layer of hydrated aluminium oxide (e.g. a quality with the designation CTG-SG from Aluminum Corp. of America) or a mixture of the mentioned hydrated aluminium oxide and aluminium hydroxide. Such a mixture can be produced by suspending 25 parts by weight of the hydrated oxide in 5000 parts by weight of hot water and by mixing the bottom phase thus formed with 100 parts by weight of the above described suspension of $Al(OH)_3$. After this mixture has been sucked through the support matrix, it is suitable also to suck up through the support matrix that solution, formed and decanted above the bottom phase, which is obtained when suspending the oxide in the hot water.

Instead of the silicon dioxide used in the above-noted

example, the layer 11bb may be a layer of titanium dioxide applied from a water suspension produced by hydrolysis of titanium chloride in water and neutralized with caustic soda to a pH of 1.5, or a layer of zirconium dioxide applied from an aqueous suspension produced by dissolution of zirconium oxide chloride in water, precipitation of the zirconium oxide occurring with caustic soda to a pH of 5.5 and acidification with hydrochloric acid to pH of 1.5. It is also possible to use commercially available colloidal solutions (e.g. a colloidal solution of silica M-12475 from the company E Merck, Fed. Rep. of Germany).

CLAIMS

1. A dynamic membrane for separation of a liquid medium, at least substantially consisting of water, from undissolved constituents therein, comprising a liquid-penetrable support matrix with through-passages, in the passages of which and on the surface of which matrix there is arranged an inner porous water-holding layer of particles of aluminium hydroxide and/or particles of at least partially hydrated aluminium oxide with a mean particle size exceeding 0.1 micron and an outer layer arranged outside the inner layer, of colloidal particles of a substance which is at least substantially insoluble in the liquid medium and has a mean particle size of less than 0.1 micron.

2. A dynamic membrane according to claim 1, in which the particulate material in the inner layer has a mean particle size in the range of 0.5 to 5 micron.

3. A dynamic membrane according to claim 1 or claim 2, in which between the inner layer and the outer layer there is arranged at least one intermediate layer of particles of a substance which is at least substantially insoluble in the liquid medium and has a mean particle size which lies between the mean particle sizes of the particulate materials in the inner and outer layers.

4. A dynamic membrane according to claim 3, in which the particles in the intermediate layer have a mean particle size in the range of 0.1 to 0.5 micron.

5. A dynamic membrane according to any one of claims 1 to 4, in which the pore sizes in the inner layer lie in the range of 0.1 to 1 micron.

6. A dynamic membrane according to any one of claims

1 to 5, in which the pore sizes in the outer layer lie in the range of 0.005 to 0.1 micron.

7. A dynamic membrane according to either of claim 3 or claim 4, in which the pore sizes in the intermediate layer lie in the range of 0.02 to 0.5 micron.

8. A dynamic membrane according to any one of claims 1 to 7, in which the outer layer comprises silicon dioxide.

9. A dynamic membrane according to any one of claims 1 to 7, in which the outer layer comprises titanium dioxide.

10. A dynamic membrane according to any one of claims 1 to 7, in which the outer layer comprises zirconium dioxide.

11. A dynamic membrane according to claim 3 or claim 4 or any claim dependent thereon, in which the intermediate layer comprises silicon dioxide.

12. A dynamic membrane according to claim 3 or claim 4 or any claim dependent thereon, in which the intermediate layer comprises titanium dioxide.

13. A dynamic membrane according to claim 3 or claim 4 or any claim dependent thereon, in which the intermediate later comprises zirconium dioxide.

14. A dynamic membrane substantially as hereinbefore described with reference to, and as illustrated in, Figure 3 or Figure 4 of the accompanying drawing.

15. A separation device incorporating a membrane as claimed in any one preceding claim.

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